Final report for

Program Title: **Chemical Reaction Dynamics in Nanoscale Environments**

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Program Scope:

The major focus of the research in this program is the study of the behavior of molecular systems confined in nanoscale environments. The goal is to develop a theoretical framework for predicting how chemical reactions occur in nanoscale environments. To achieve this goal we have employed ab initio quantum chemistry, classical dynamics and quantum dynamics methods. Much of the research has focused on the behavior of molecules confined within single-walled carbon nanotubes (SWCNTs). We have also studied interactions of small molecules with the exterior surface of SWCNTs. Nonequilibrium molecular dynamics of interfaces of sliding surface interfaces have also been performed. Much of the work has been completed, but there are still papers being written and work being performed that will result in publications acknowledging funding from this Department of Energy grant. We expect that this will result in at least four more publications, three of which are currently in the progress of being written up.

Accomplishements:

The Goldfield group focused on research into the behavior of hydrogen molecules confined within SWCNTs of various shapes and sizes. Quantum mechanical energy level were computed for the hydrogen molecule and its homonuclear isotopomers confined within nanotubes of various sizes and (SWCNTs) of various shapes and sizes. These studies were the first to treat translation and rotation together. Using different interaction potentials, studied the dependence on the interaction potential and the size of the nanotube of several quantities including zero-pressure quantum sieving selectivities for isotopes and also for neutron spin states, ortho-para energy splittings and characteristics of the energy levels. We show that large quantum sieving selectivities as well as large deviations from gas phase ortho-para splittings occur only under the condition of extreme two dimensional (X2d) confinement, when the characteristic length of the hydrogen-carbon interaction potential is nearly equal to the radius of the nanotube. Under these conditions, we see very dramatic effects on rotational structure: extreme two dimensional confinement. The results of this research have been published.

Current work is focused on the calculation of the interaction of H + H_2 within SWCNTs of various sizes. We have recently completed a quantum study of this reaction. Because the transition state of this reaction is collinear, it is possible that the restricted geometries permitted within the nanotube would enhance the reaction probability. It is also possible however that hydrogen atoms close to the walls of the nanotube will react strongly with the nanotube carbons. Therefore, we ran wavepacket calculations to see whether H atoms at

one end of a nanotube with momenta directed along the central tube axis were capable of traveling through to the other end of the tube. Portions of the wavepacket that were attracted to the walls were absorbed. We computed the distance traveled as a function of tube diameter and initial wavepacket momentum. Not surprisingly, the larger the tube, the more wavepacket density reached the other end. But, except for the smallest tubes studied, a large portion of the hydrogen did emerge on the other end of the tube. Since we are interested in the effects of the geometrical restrictions, we did not include this short range reactive potential in the quantum calculations of this reaction.

The $H + H_2$ quantum calculations have been computed using a simplified model for the reaction that focuses on the most important degrees of freedom .We explicitly treat the there internal degrees of freedom of H_3. Motion relative to the nanotube is modeled with one rotational and one translational coordinate. The major finding of this research, which is currently being written up, is that the reaction probability is indeed enhanced by confinement within nanotubes and the enhancement is increased as the tube diameter is reduced. We are now engaged in a classical trajectory study of this reaction in realistic nanotube models. This study will contain three different calculations of increasing complexity: 1) we will use the same interaction potentials that we used in the quantum study, 2) we will turn on the short range potential that permits the H atom to interact with the nanotube carbons and 3) we will permit the nanotube carbons to move also.

The Goldfield and Schlegel groups engaged in preliminary studies of the binding of small molecules such as NO2 to the outer and to the inner walls of semi-conducting SWCNTs. This work was in conjunction with a member of our computer and electrical engineering department who is developing a nanotube based chemical sensor. The interaction between NO_2 and a finite length (20 Å) semi-conducting (10,0) carbon nanotube ($C_{200}H_{20}$) was studied at the PM3, Hartree-Fock and density functional levels of theory. Semi-empirical calculations show that NO_2 adsorbs on the carbon nanotube; however, the spin unrestricted calculations have a very large spin contamination and therefore quantitatively give wrong values for band gap after NO_2 adsorption. Spin restricted open shell Hartree-Fock (ROHF) calculations give more reasonable energetics and charge distributions. We also used naphthalene and pyrene as "models" for SWCNTs and studied the interaction of two NO_2 molecules with these molecules at the B3LYP level of theory in chemisorbed as well as physisorbed configurations A mechanism for formation of NO_3 on the small molecules was also investigated at B3LYP level, which will be subsequently investigated on the (10,0) finite sized nanotube. Unfortunately, before this work could be completed, the graduate student (Deepti Phatak) left to take a job in industry. The work will be resumed when we find a suitable student to undertake it.

The dissociation of formaldehyde confined in a carbon nanotube has been studied in the Schlegel group using QM/MM methods. The nanotube was treated with the UFF molecular mechanics force field and the H_2CO was treated quantum mechanically (HF/3-21G level of theory).The calculations provide a greater insight into the effect of a constrained environment on the dissociation dynamics. Both CO and H_2 show a greater extent of vibrational excitation compared to the gas phase dissociation with vibrational levels up to v=5 being populated in the H_2 fragment. Compared to the gas phase dissociation, the rotational distribution occurs at lower values of J for CO and at higher values of J for H_2.

Collisions of the fragments with the walls of the tube could account for the higher rotational and vibrational levels of the H_2 being populated. Similar to the gas phase dissociation, product translation received most of the available energy. This research is currently being written up for publication.

The Schlegel group has completed a study of the of ionization potential (IP) and electron affinity (EA) of molecules within SWNT's. Whether the molecule or the tube will gain or loose an electron depends on the relative IP's and EA's of the molecule and the carbon nanotube, and on the stabilization resulting from their interaction. Because carbon nanotubes are highly polarizable, they stabilize cations and anions more than neutrals. Thus, when a neutral molecule is placed inside a carbon nanotube, or in close proximity to one, its ionization potential will be lowered and its electron affinity will be increased by as much as 1 eV. A series (7,7) armchair nanotubes ranging in length from 13-30 Å as well as (8,8) and (9,0) nanotubes of ca 15 Å length were calculated at the B3PW91/3-21G level of theory and the molecules within them were calculated at the B3PW91/6-311++G(d,p) level. The IP's and EA's of carbon nanotubes vary with length more than with diameter and can be understood in terms of simple Hückel theory. Five categories can be identified for the ionization of a molecule + carbon nanotube system: (i) the molecule always ionizes but the nanotube does not, (ii) the nanotube always ionizes but the molecule does not, (iii) the molecule ionizes spontaneously as soon as it is placed inside the nanotube, (iv) the nanotube ionizes spontaneously as soon as the molecule is placed inside, and (v) either the molecule or the nanotube ionizes, depending on the length of the tube. Most neutral molecules with high IP's and low EA's fall into case (ii). Atoms and molecules with very low IP's, such as alkali metals, are examples of case (iii). Halogens and molecules with high EA's can serve as examples for case (iv). Because the nanotubes have low IP's and high EA's, and because nanotubes strongly stabilize molecules within them, no example could be found for case (i) for the nanotubes in the present study. The CN radical is an intriguing example of case (v). Because the IP oscillates by more than 0.5 eV as the length is incremented, the electron is removed from CN for some lengths and from the nanotube for other lengths. This work has been published.

Nonequilibrium molecular dynamics simulations were performed in the Hase research group to study the dynamics of energy transfer at the interface of a small nanoscale hydroxylated alpha-alumina surface sliding across a much larger surface of the same material. Nonequilibrium energy distributions were found at the interface for each of the conditions studied. The velocity distribution P(v) for the atoms in a sublayer of the smaller surface oscillates during the sliding, reflecting the periodicity of the interfacial intermolecular potential. When averaged over the sliding, this P(v) for each of the sublayers is bimodal with Boltzmann and non-Boltzmann components. The non-Boltzmann component, with temperatures in excess of 1000 K and as high as 2500 K, is most important for the interfacial H-atom sublayer and becomes less important in moving to a sublayer further from the interface. Similarly, the temperature of the Boltzmann component decreases for sublayers further from the interface and approaches the 300 K temperature of the boundary. The temperature of the Boltzmann component decreases, but the importance of the non-Boltzmann component increases, as the sliding velocity is decreased. The temperature of the non-Boltzmann component is relatively insensitive to the sliding velocity. Friction forces are determined by calculating the energy dissipation during the

sliding, and different regimes are found for variation in the friction force versus sliding velocity v(s) and applied load. This work has been published.

A molecular dynamics simulation was performed to study the effect of an applied force on heat transfer at the interface of model diamond {111} nanosurfaces. The force was applied to a small, hot nanosurface at 800, 1000, or 1200 K brought into contact with a larger, colder nanosurface at 300 K. The relaxation of the initial nonequilibrium interfacial force occurs on a subpicosecond time scale, much shorter than that required for heat transfer. Heat transfer occurs with exponential kinetics and a rate constant that increases linearly with the interfacial force according to $7 \times 10^{-4} ps^{-1}/nN$. This rate constant increases by at most 10% as the temperature of the hot surface is increased from 800 to 1200 K. Replacing the interfacial H-atoms on both surfaces by D atoms also has a very small effect on the heat transfer. However, if one nanosurface has H atoms on its interface and the other nanosurface's interface has D atoms, then there is a marked 25% decrease in the rate constant for heat transfer. Increasing the size of the hot surface, and thus the interfacial contact area, increases the rate of heat transfer but not the rate constant. For the same interfacial force, different anharmonic models for the nanosurfaces' potential energy function give the same heat transfer rate constant. The results of these studies have been published.

Additional research in the Hase group include a preliminary and unpublished simulation performed by Tianying Yan to study the dynamics of alkyl thiol self-assembly on a gold surface in nanografting experiments.[1] In these experiments a bare substrate region is prepared by using an AFM tip to displace thiols. Spatially confined regions are formed into which an alkyl thiol with a different chain length adsorbs. The kinetics for adsorption into this confined region is different than for a completely bare surface.[1] Trajectories were used to simulate the adsorption of alkyl thiol chains into such a confined region, and it was found that this confinement enhanced the efficiency of the chain ordering and self-assembly.

When a chemical reaction takes place in solution atomic motions of the reacting molecules are confined by their interactions with the solvent. Of particular interest is how this confinement affects the course of the reaction and energy dissipation as the reactive system moves from a high energy transition state towards different possible products. Lipeng Sun compared Wigner and quasiclassical sampling methods for choosing initial conditions in a trajectory simulation and found that they give similar results. This work will be published.

In summary, we have completed research on the behavior of small molecules confined in SWNT's, on effects of confinement within SWNT's on chemical reactivity and on the ionization potentials and electron affinities of confined molecules. We have simulated energy transfer and heat transfer at the interfaces of small nanosurfaces and larger ones. We have gained a better understanding not only of confinement effects but also a greater appreciation for the subtleties involved in these types of calculations.

1. S. Xu, P. E. Laibinis, and G.-y. Liu, *J. Am. Chem. Soc.* **120**, 9356 (1998).

Publications of DOE Sponsored-Research:

1. T. Lu, E. M. Goldfield and S. K. Gray, "Quantum states of hydrogen and its isotopes confined in single-walled carbon nanotubes: Dependence on interaction potential and extreme two-dimensional confinement**"** J. Phys. Chem. B **110** , 1742 (2006)
2. J. E. Knox, M. D. Halls and H. B. Schlegel, "Guest species / discrete carbon nanotube inner phase charge transfer and external ionization ", J. Comput. Theor. Nanosci. **3**,396, 2006
3. O. A. Mazyer and W. L. Hase, "Dynamics and kinetics of heat transfer at the interface of model diamond {111} nanosurfaces", J. Phys. Chem. A **110**, 526 (2006)
4. O. A. Mazyar, H. Xie and W. L. Hase, "Nonequilibrium energy dissipation at the interface of sliding model hydroxylated α-alumina surfaces", J. Chem. Phys. **122**, 094713 (2005)
5. T. Lu, E. M. Goldfield and S. K. Gray, " The equilibrium constants for molecular hydrogen in carbon nanotubes based on iteratively determined nano-confined bound states", J. Theor. Comp. Chem., special issue on Iterative Methods in Quantum Mechanics and Applications to Chemical Problems" **2**, 621 (2003)
6. T. Lu, E. M. Goldfield and S. K. Gray, "Quantum states of molecular hydrogen and its isotopes in single-walled carbon nanotubes ", J. Phys. Chem. B **107,** 12989 (2003)

Manuscripts in Progress:

1. T. Lu, E. M. Goldfield and S. K. Gray **,** "Effects of confinement in a nanoscale cylinder on the reactivity of $H + H_2$: a quantum dynamics study"
2. T. Lu, E. M. Goldfield and S. K. Gray, "Classical trajectory study of $H + H_2$ confined in single walled carbon nanotubes"
3. S. Anand, E. M. Goldfield and H. B. Schlegel, "Dissociation of formadedyde ($H_2CO_2 \rightarrow H_2 + CO$) confined with a single walled carbon nanotube"